Chapter 7

Polymeric Membrane for CO₂/CH₄ Separation

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Abstract

This chapter presents a critical overview of polymeric membrane applications for CO₂/CH₄ separation. Comparative summary of availability and practice of different gas separation methods are outlined to give a state-of-the-art view of this technology. Detailed discussions on polymer-based membranes are also discussed in this work, highlighting the mechanism of selective gas permeation through the membranes. Future direction is discussed for possible new experimental design to maximize the membrane performances in separation of CO₂/CH₄.

Keywords

Polymeric Membranes, Gas Separation, Membrane Technology, CO₂ Capture, Methane

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1. Introduction

Currently, the volume of greenhouse gases (GHG) in the air has increased dramatically [1]. Consequently, the accumulation of CO₂ in the atmosphere has generated much interest in the development of various techniques for the separation of CO₂ from fuel gases. Firstly, the gas separation process through a polymer has been discovered in 1892 by Thomas Graham. The polymeric membrane has been utilized in gas separation process for energy efficiency and affordability. Despite that, its incompetence to withstand high temperatures restricts their utilization in the industries [2]. In addition, polymeric membranes with permeances above 1,000 GPU and selectivity index over 30 are excellent properties for CO₂ capture from flue gases [3-5]. However, the separation of CO₂/CH₄ is likewise a notable industrial procedure. It exhibits an approximately 20% of the annual natural gas in United States (U.S.). It has unmistakably demonstrated the cost of funding and operational separation process, where numerous drawbacks have been observed at a higher concentration of CO₂ (over 2%), especially in the pipeline; for example, pipeline corrosion and declining heat rate of natural gas [6].

Some polymer membranes can function at certain levels of uncondusive surrounding, yet the energy with the economic performance are counterbalanced by the need to reduce the temperature of hot streams severely. On several occasions, similar performance is inconceivable or entirely unfeasible. Thus, various researches have stressed upon the alteration of polymers to produce synthetic polymeric membranes that can endure extreme temperatures [7-9]. Fig. 1 shows the different approaches to improve polymeric membrane materials [10].

Figure 1. Few methods of membrane modification to enhance properties of polymeric membrane.

Referring to Fig. 1, there are several techniques that can be implemented onto polymeric membranes, such as surface modification, blending process, introduction of new additives, and cross-linking methods. For example, in blending process, polymeric membrane can be simply prepared by the dispersion of inorganic materials into organic solvents, such as N-methyl-2-pyrrolidone (NMP) and dimethylformamide (DMF) [11]. The blending of these two materials will yield larger polymeric/particles interfacial area that will be beneficial towards the percentage loading of the inorganic nanomaterials into the polymer matrix. Researcher presented different thermal stable polymers, especially on carboxylic and heterocyclic aromatic polymers, which showed an increase in temperature stability [2]. Fundamentally low probability of the polymers has shown significant issue because of their insolubility or long-term conversion temperature. Consequently, by far, small accomplishment has been observed in the handling of high thermal resistance polymers to produce membranes with adequate separation and performance attributes.

Issues such as expensive inorganic membranes, porous hybrid materials, and modularization lead to numerous researches that focus on modifying the polymers to

develop synthetic polymeric membranes with high thermal resistance. Polymeric membranes are cheap and it can be further fabricated within vast-scale modules. Subsequently, employing polymeric membranes for gas treatment has partaken an everyday practice in numerous industries [12]. Nonetheless, shortage of resilience toward high temperature is one of the real constraints of the modern polymeric material. Due to some of these streams which cannot be exposed to the course of membrane separation, many hot gas streams in each chemical industry have to be held at an elevated temperature during the gas separation process. In particular, the process flow temperature is reduced merely to adjust the cycle gas separation membrane, then reheated and coupled with heating and cooling, all of which leads to a great deal of energy abuse. In considering offshore structures and reservoir comprising large amounts of CO₂, the use of this innovation was observed to be entirely beneficial, as it is a proficient framework with a basic moderate procedure in spite of the motion conditions. All energy sources until the middle of 21st century, which is in conjunction with the projection of world energy consumption, has presented natural gas, yet it remains outdistanced from the others. It includes the synchronous confrontation of CO₂ separation from natural/biogas (acid gas removal), along with succeeding trap of CO₂ transmitted from power plants (to mitigate climatic change due to CO₂ emission) [3].

Using membrane technology, gas separation has significant benefits amid the progress of other CO₂ separation techniques, such as refining, adsorption, and cryogenic absorption. Membrane production with permeability and selectivity is one of the major motivations behind membrane-based gas separation studies. Hasebe and co-workers [13] reported the permeability of CO₂ and selectivity of CO₂/N₂ separations via mixed matrix membranes (MMMs) comprised of polymer and nanosized silica particle, having nano-space gas permeance (Fig. 2). Although polymeric membranes offer various benefits, such as the ability to produce significant medium-sized membrane areas with minimal cost, some issues still exist, which are related to the trade-off relation between gas selectivity and gas permeance [14, 15]. As a result, the membranes usually have an upper limit. Although there are many possible uses for polymer membranes in gas separation, most membrane materials are out of phase due to the expensive materials used. Therefore, to this day, continuous efforts have been made to find alternative materials for effective CO₂ separation. Various techniques have been examined to improve the performance of specific membranes; for instance, blending, cross-linking, grafting, mixing with suitable additives, and etcetera [16].

Figure 2. Selectivity of gas pairs CO_2/N_2 using MMMs made up of polymer and silica nanoparticles. Reproduced with permission from [13].

A membrane is portrayed explicitly of perm-selectivity of molecules passing through [17]. It is important to note the permeation flux is influenced by membrane structure and gas transport process driven by its potential chemical gradient. Thus, the selectivity is taken into account as an inconsistency of flux between the penetrants [18]. Membrane technology for gas separation has become drastically expended in recent decades; hence, the development owed to the rapid growth of progressively effective membrane with higher perm-selectivity. Economic advantages of the hydrogen recovery are prompted quickly in the establishment of a few frameworks around the globe [19]. Separation of gas using membrane has been established in different fields, for example, in the removal of CO_2 from natural gas, N_2 from air, as well as H_2 from various plant refineries and petroleum processing streams [20]. To add in the list, the separation of CH_4 from biogas, O_2 -enrichment for further applications in metallurgy or medical area, and the removal of volatile organic liquid (VOLs) from exhaust streams are also utilized in various membrane technologies [21]. The advantage of choosing a membrane in the field of gas separation is that it is cost effective, has high efficiency, easy to use, has modularity, and is easy to scale up. Most importantly, membrane separation is a continuous process for ensuring efficient gas separation. Furthermore, classical materials could be used in the industry even though there are many numbers of new materials utilized in the membrane separation innovation. Processes of gas separation by membrane are usually considered to be in a steady-state.

It is essential to test the gas flowrate and gas inlet composition amid the task. In such event, the composition of the end-product needs to be maintained consistently during the dynamic procedure control framework throughout the separation procedure. In most

cases, steady membrane permeance frequently opted for effortlessness for the simulation. Bounaceur et al. [22], in their work studied the permeance of gas mixture at different processing pressure, which was dependent on the solution-diffusion model. From the results, it was found that the consistency of permeance can cause significant problem for the membrane during the separation of CO₂/CH₄. The Bounaceur groups stated that if the difference in CO₂ concentration between the gases in and out is greater than 1%, the assumption made on the membrane permeability model is not accurate enough to estimate the gas separation performance for certain types of membranes.

2. Polymeric membrane for CO₂/CH₄ separation

2.1 Polyimides

In general, polyimide (PI) can potentially act as a membrane material with promising separation performance. They have high chemical stability and are stable at high temperature condition, compared with other polymers, making them preferable for utilization in commercial applications [23]. However, as mentioned by Favvas et al., PI, which is classified as glassy polymers tends to suffer physical aging similar to other polymers in the same group [24]. In addition, the existence of CO₂ in gas mixtures will create strong plasticization of this polymer, thus directing to low selectivity in gas separation process. To address this issue, cross-linking or fabrication of hyperbranched polymer structure is needed. Hyperbranched of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 4,4'-triaminotriphenylmethane (TTM) on PI membrane had improved the CO₂/CH₄ separation selectivity value of 137 [25]. In another work by Zhang et al., the cross-linked PI has been successfully fabricated with 6FDA-carboxylic acid-containing diamines (CADA1), having superior CO₂/CH₄ separation performance with a selectivity value of 48 [26]. On top of that, the cross-linked 6FDA-PEG on PI membrane yielded high selectivity of CO₂/CH₄ with a value of 46 [27].

(a) *Matrimid*[®]

Matrimid[®] 5218 is one of the commercial PI that is currently used in CO₂/CH₄ separation due to its good thermal and mechanical stability, high solubility in solvents, and excellent processability for membrane casting process [28]. Additionally, it has good selectivity but poor CO₂ permeability. However, the permeability can be improved by the incorporation of polyethylene glycol (PEG) as an additive and via the addition of nanoparticles, such as zeolitic imidazolate framework (ZIF). Compared with pristine Matrimid[®], the selectivity CO₂/CH₄ of Matrimid[®]/PEG/ZIF was higher, with the value of 25.08 (pristine Matrimid[®] = 17.40) [29]. The selectivity of CO₂/CH₄ was enhanced at about 66% (selectivity = 36.3) and 57% (selectivity = 57.1) for Matrimid[®]/zeolite-Y and

Matrimid[®]/NaY-zeolite, respectively [30, 31]. The blended Matrimid[®] membrane and 1-ethyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide ([Emim][Tf₂N]) as an ionic liquid (IL), as presented in Fig. 3, has been fabricated for separation of gas mixture CO₂/CH₄ [32]. Permselectivity of CO₂/CH₄ had improved to 96% (from 32 to 63). The IL is believed to have improved the diffusivity coefficient, which resulted in higher permeability and permselectivity, compared with bare Matrimid[®]. In another work by Rajati et al., the MIL-101(Cr) was added as a filler in the Matrimid[®]/PVDF blended membrane [33]. From the final results, selectivity of CO₂/CH₄ of blended MIL 101(Cr)/Matrimid[®]/PVDF was found to be higher, with the value of 61.95, compared with the unblended Matrimid[®] (selectivity = 34.90). The uniform dispersion of MIL 101(Cr) in Matrimid[®]/PVDF could have enhanced the permeability of CO₂/CH₄ separation.

Figure 3. The preparation of blended Matrimid[®]/IL membrane. Reproduced with permission [32].

2.2 Polysulfones

There are three main types of polysulfone (PSF)-based membranes that are commercially used in CO₂/CH₄ separation, which is dense, asymmetric, and composite polysulfones. Both dense and asymmetric-based PSF membrane consist only PSF. Meanwhile, composite PSF-based membrane is made up of PSF incorporated with other types of

polymers. The fabrication of PSF-based membrane can be done via dry, wet or dry/wet process [34]. In brief, the preparation of the PSF-based membrane involve the immersion, coagulation, and phase separation process of binary mixture between a polymer and selected solvents [35]. In terms of CO₂/CH₄ separation performance, PSF-based composite membrane can significantly improve the selectivity of the gas separation. As studied by Hatami et al., by using Pebax/PSF membrane with ZIF-90 as additives, the selectivity of CO₂/CH₄ was able to reach a value of 75.05 [36]. Mohamad et al. prepared PSF membrane incorporated with zeolite-T via priming method [37]. They found that the addition of 4 wt% loading of zeolite-T into polysulfone content a highest CO₂/CH₄ ideal selectivity of 3.37 from 2.63 due to the agglomeration of zeolite-T in polymer matrix. Polydimethylsiloxane (PDMS)/PSF membrane has been fabricated via dip coating method for CO₂/CH₄, resulting in a selectivity value of 85 [38]. Additionally, Suleman et al. mentioned that the water swelling in PDMS/PSF membrane had initiated contraction in the membrane pores, thus dramatically increasing the CO₂/CH₄ selectivity. Report from another researchers, Kiadehi et al. stated that carbon nanofibers (CNF)/PSF mixed matrix membrane exhibited a selectivity value of 12.17 for CO₂/CH₄ [39].

2.3 Polyetherimides

Other than PI, as visualized in Fig. 4, polyetherimides (PEI) is the one of the common classes of polymers that is widely studied for separation of gas by membrane due to their superior properties [40]. However, both of these polymers are facing serious problems attributed to the plasticization effects. These effects can be minimized by introducing several techniques, including cross-linking and surface modification via the addition of certain functional groups at the polymer backbones to alter the chain packing, which subsequently results in free volume increment. The effect of PEI-backbone modification has been investigated by Madzarevic et al., proving that the modified 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA)/PEI membrane had improved the CO₂/CH₄ selectivity value of 70 compared with that of pristine PEI [41]. In another modification, zeolite SAPO-34 incorporated with PEI membrane presented an ideally high CO₂/CH₄ selectivity of 60 [42]. Recently, the modification of PEI membrane was done via the blending technique with carboxylated carbon nanosheets [43]. Interestingly, the carbon nanosheets are produced from biomass-derived of monkeypod tree leaves. Based on the final analysis, the gas separation had a selectivity value of 42.73 for CO₂/CH₄, compared with bare PEI membrane at 23.30 [44].

Figure 4. The chemical structure of PEI. Reproduced with permission from [40].

2.4 Polyethylene glycol

Polyethylene glycol (PEG) acts as a stabilizer of the liquid polymer in the polymer phase. The previous studies proved that an ethylene oxide unit in PEG as plasticizer is beneficial, as it can increase CO₂ permeability and therefore improve the selectivity of CO₂/nonpolar gases. The addition of nanoparticles into PEG-based membrane was able to increase the adsorption capacity of CO₂. As reported by Azizi et al., the addition of TiO₂ nanoparticles into PEBAX-1074/PEG-400 had a superior selectivity of CO₂/CH₄ value at 23.61 [45]. Noroozi et al. investigated amino- TiO₂ incorporated within blended PEBAX-PEG membrane, which then resulted in CO₂/CH₄ selectivity enhancement by 16.6 [46]. Gharibi et al. prepared a hybrid organic-inorganic poly(urethane-siloxane) membrane with built-in PEG for CO₂/CH₄ separation performance [47]. Two different contents of PEG (55 wt%, 71 wt%) were used, and the work reported that PEG of 71 wt% showed a better selectivity of CO₂/CH₄ at 20.8, compared with that shown by PEG of 55 wt%.

2.5 Classical membranes and their disadvantages

In comparison with the typical process, membrane gas separation uncovers particular benefits, as well as high proficiency, inexpensiveness, and ecological effect [48]. Despite that, the principle issues of current polymeric membranes are the confinement of permselectivity (possibilities to process low gaseous volume at under 30 million of standard cubic feet daily), with poor thermal-chemical balance, and surrender to plasticization effects. Thus, every small advance in the manufacture of gas separation membranes incorporates a significant amount of money savings, which makes the membrane a prominent presence in the industrial gas separation [4]. Presently, there is a rise in the mass uptake (adsorption) of CO₂, H₂O, H₂S, and higher hydrocarbons referred to as condensable penetrants. Swelling within the conventional polymer membrane will thus expand the polymer free volume (dilation) with its segmental versatility. A phenomenon subjected as "penetrant-induced plasticization" or "plasticization" shall either enhance or more

commonly diminishes the gas diffusivity selectivity [49]. Plasticization frequently leads in higher CO₂ gas flux but lower CO₂/CH₄ and CO₂/N₂ gas selectivity of conventional membrane materials polysulfides, especially at high pressure. For plasticized and glassy polymeric membranes, typically, the gas permeability is reduced at a higher feed pressure up until plasticization takes place. Subsequently, it will begin to expand with increasing pressure. Induced plasticization process in glassy polymers also known as "plasticization pressure", is carried out between 10 to 35 bars for polymers related to gas separation with regard to CO₂. These measurements are different from the equilibrium value for low upstream pressure, which include increments in time. By now, dependent relaxation process of the polymer stated to contain the basics of non-equilibrium glassy condition of a polymer. It is also expressed that the penetrated molecules swell and consequently, slackens the matrices of polymer, which brought about the suppression of glass transition temperature, T_g [50, 51].

As shown in Fig. 5, it is seen that it portrays the external plasticization and internal plasticization, where (a) shows plasticizers that are not bound to any polymers, and (b) shows plasticizers that are bound to polymers. Thermal treating has been aforementioned [52], hence, the remaining two will be considered thereafter. Apart from reducing the plasticization effects, frequent blending enhances the properties of polymeric membranes in terms of their mechanical and thermal strength, as well as their separation performance [53]. Moreover, it encourages the transportation of a particular gas, which can be accomplished by altering the blend composition and observing the resulting morphologies of the membrane [54, 55]. In several cases, a blend that is able to separate the different phase material is needed for the sake of species transport [56]. Miscible/homogeneous type of blends is better suited for expanding the gas selectivity while drastically improving the permeability performance. Free volume polymer extension takes place amid the mixing procedure of immiscible blends, causing higher gas permeation rates. However, a significant negative volume change in the mixing of homogeneous miscible polymer blend had led to a notable reduction in gas permeation rates and therefore, an expansion in gas selectivity [57, 58].

Figure 5. External plasticization and internal plasticization where (a) shows plasticizers that are not bound to any polymers and (b) is plasticizers that are bound to polymer. Reproduced with permission from [52].

2.6 Polymeric membrane for gas separation: mechanism and efficiency

The separation of CO_2/CH_4 across polymeric membrane can occur through several transport mechanisms. Fig. 6 exhibits five main types of mechanisms of gas transport through the membrane, namely: capillary condensation, Knudsen diffusion, molecular sieving, solution-diffusion mechanism and surface diffusion [59]. These mechanisms are applicable for various types of gases that are highly dependent on the characteristics of the membrane, especially on the size of membrane pores. Occasionally, mixing of cross-linking and blending is opted to accomplish a superior quality. For instance, the CO_2 -selective membrane of PVA blended with PVP incorporated with appropriate amine carriers has been synthesized by Mondal and Mandal [60]. Formaldehyde was applied as the cross-linking agent, where it resulted in high CO_2/N_2 selectivity of 370, with CO_2 permeability of 1396 Barrer at a temperature of 100°C and 2.8 atm. The latest methodology was established as hybrid ternary blends, whereby it implies the suitability of the blend constituents by the add-on of specific additives.

Figure 6. Gas separation mechanism through polymeric membrane. Reproduced with permission from [59].

Apart from having the ability to improve the mechanical properties, another aspect of the specific fillers is that is able to induce a great decline in plasticization of the blends [61]. Cross-linking of membrane material at high temperatures ($\sim 15^\circ\text{C}$ above T_g) for polyimide-based membranes was demonstrated by Qiu et al. (2011) [51]. The composite is capable of balancing out the membranes in regard to the swelling and plasticization effects in aggressive feed streams. It should be noted that at a raised temperature, it could lead to the breakdown inside the matrix membrane, which includes the substructure and transition layers in membranes. The sub- T_g cross-linking outcome demonstrated that the cross-linked membranes selectivity could be kept even at tough CO_2 working condition, which is impractical without cross-linking. Additionally, the plasticization pressure denotes the maximized feed pressure beyond which glass polymer-typed membrane can no longer operate profitably [62]. Mixing of cross-linking (GC) and grafting was further revealed as an enhanced procedure to inhibit plasticization. The altered membranes conserve a precisely similar selectivity to that of CO_2/CH_4 , which is in contrast with the unaltered form. Nonetheless, the pure CO_2 permeability of 139 Barrer was acquired in an excess level of magnitude, as compared with the neat CA polymer.

The CO_2 separation research industry has its focus on evolving the separation techniques of polymeric membranes. Since membranes are competing with other separation industries, efficiency will be dependent on safety, environment, economic, and technologies prospects [63, 64]. Hence, enhancing polymeric membranes by increasing the permselectivity can shorten the high expense of membrane innovation. Thus, one

needs to concentrate on the present challenges by presenting new polymeric membranes that can carry higher CO₂ permeability, combined with adequate selectivity and has great physical and chemical strength. By far, in manufacturing gas separation membranes, various polymers have been utilized, especially poly(pyrrolone), polyacetylenes, poly(ethylene oxide), polysulfones, polyaniline, polyacrylates, poly(arylene ether), polyimides, polycarbonates, polyetherimides, and poly(phenylene oxide) [65]. The utilization of these materials has drawn much research attention. Several primary issues in the area are thermal and pressure of the system, plasticization, and traces of contaminants, permeation hysteresis, casting solvent, and physical and chemical aging. Current studies are committed to clarifying concerning matters influencing the CO₂ separation properties of established polymeric membranes. Apart from that, further classes of CO₂ separation performance polymeric membrane are outlined. Polymers having characteristics such as microporosity (PIM) [66], thermally-rearranged polymers [67], PI [68], and polyurethanes are a few examples of membranes that display higher efficacy for CO₂ separation [69]. Consequently, the industry is convinced that the above-mentioned elite membranes will be able to isolate the different CO₂-containing gas mixtures. In the future, CO₂ permeable membranes shall concentrate on upgrading these economically effective polymers by increasing the awareness on industrial applications.

Nevertheless, the advancement of CO₂ permeable materials is beginning to become a concern towards conventional polymeric membranes. Even though cellulose acetate membranes are widely utilized, more recent membranes, for example, PI membranes, have been manufactured and marketed by the Air Liquide Medal Company. One of the causes is the presence of flux within cellulose acetate membranes, which diminishes considerably with time due to plasticization (response among CO₂ and polymeric chain) and compaction of material (poor mechanical quality) [70, 71]. In reality, the existence of differential pressure inside the membrane will prompt the breakdown of the pores, reducing the bare regions to flow, which later influence the performance of membrane. PI membranes are less responsive but have higher resistance; the mentioned membranes are gradually substituting cellulose acetate. It is only essential to show proof of product contribution to the industry involved when introducing new technologies to the market [53]. To verify an enduring and productive future of an alternative system, one must ensure it can be viewed as a sustainable technology. On the subject related to sustainable development, knowledge on the general definition of concept is vital. In spite of obvious words such as "green" or "eco-friendly", which may have been utilized in the early stage of developing a sustainable technology, the present definition has been used for the ecological sphere enclosing economic and social concepts. Nowadays, innovation is not determined only based on its effectiveness, cost, and other performance-oriented

problems, rather, on its environmental effect and future social impact, which are deemed to be likely very significant factors [71]. Those three spheres (economic, ecological, and social impacts) are related, can be observed with a substantially intricate investigation on the consequences of a new project. In the modern world, it is without a doubt that there may be occasions that prevail one sphere over the other, for instance, over the economic sphere; nonetheless, the remainder elements still bear a considerable weight in a decision-making process.

It is conceivable to distinguish research patterns oriented to every three parameters concerning relatively latest membranes innovation. One would be regarded as oblivious to expect that the oil industry would put its attention to the system while considering its benefit involvement with environmental and social ideas [72]. However, there are some slight advantages that can be observed; unmistakably, the industry target is aimed towards profit increment and the making of significant worth. The membranes innovation employed to CO₂ productive oil production wells will allow an effective gas separation into two essential streams: methane-rich stream and carbon dioxide-rich stream. The later stream is utilized to improve the oil recovery method, which will extend the life cycle of an oil reservoir through improved oil flow, flow properties, and/or its water-rock interaction. A major advancement in gas separation via polymeric materials for membrane was observed over the last decade [73, 74]. About several polymeric materials have been designed because of their exceptional transport properties, which makes them capable of being an energy-effective course for large-scale gas separation. These deliberate research endeavors are catalyzed by the critical need to lower CO₂ emission from the burning of fossil fuels and flue gas combustion by various plants (i.e., coal-fired power plant flue gas). It is considered a viable technological solution to alleviate the impact of climate change due to carbon dioxide emission to both economy and environment [8, 75]. The membrane, in contrast with another CO₂ separation method, is favorable due to its simplicity to operate, compactness, low energy consumption, and ability to prevent limitation of thermodynamic solubility [76]. These highlighted advantages are derived from the use the membrane as a thin, intermediate layer that acts as a selective barrier to separate the two different phases [77]. This slimness commonly scales to around 100 nanometers to some micrometers, giving a practically universal stage to actualize sophisticatedly engineered macromolecular structures. To maintain the pressure difference across membrane, feed stream compressing as in Fig. 7 can be done or alternatively, installing the permeate side with vacuum pump. Spiral-wound composite membranes have reported the recovery of 90% to 99.99%.

Figure 7. The pressure difference across the membrane can be maintained either by compressing the feed stream [78].

2.6.1 Surface functionalization

Improvement of polymeric materials with increasing permeability and CO₂ selectivity has been widely sought in the past decade. However, an important obstacle is the permeability or selectivity exchange, where high-permeability polymers generally have low selectivity and vice versa [79].

Various polymeric materials were employed for the synthesis of membranes in gas separation application, such as poly(pyrrolone), polyacetylenes, poly(ethylene oxide), polysulfones, polyaniline, polyacrylates, poly(arylene ether), polyimides, polycarbonates, polyetherimides, and poly(phenylene oxide). Several difficulties concerning the utilization of these materials have gained the interest of researchers. Some of the issues faced in the field are the thermal and pressure of the system, plasticization, traces of contaminants, permeation hysteresis, casting solvent, and physical and chemical aging [12, 16]. An abundant free volume in glassy polymers matrix is subject to change due to the current state of production, thermal history, and exposure to sorbing materials. The so-called "physical aging" that drives the nature of membrane transport depends on time mainly articulated in thin films [80]. Huang and Paul suggested a technique for monitoring physical aging of thin glassy polymer films associated with gas separation [81]. Due to physical aging the packing density will elevate and the permeability will drop drastically over the time [82].

Lately, for thickness of selective membrane that is lower than 1 micron, the job of the membrane thickness on physical aging was likewise perceived. Membranes used in gas separation frequently has a thickness below 0.1 mm, in which the effect of thickness on

aging has a significant interest in the field of study mentioned [83]. The physical and chemical aging rely upon time and temperature, as chemical aging causes changes within the chemistry of the polymeric membrane, which typically prompts membrane degradation with concurrently weakening of the properties (for example, coloration and embrittlement). Physical aging adjusts the local packing of the chains, yet results in no adjustments in the polymer structure. Hence, only the measurements and physical properties of the polymer, such as T_g , tensile strength, and brittleness, were modified. In this manner, the fundamental contrast among both impacts is that physical aging is a reversible procedure, but chemical aging is not [50, 84, 85]. It compromises the two "anti-aging" methods, including:

- ❖ Solidifying the free volume state setup employing inorganic or organic non-porous or porous fillers in enhancing free-transport pathways; and
- ❖ Utilizing cross-linking, copolymerization, and surface plasma treatment to strengthen the setup of first polymer structure.

The added material cannot adequately compensate for FFV to minimize aging, although cross-linking can effectively stop aging; however, drastic decrease in gas permeance was observed [86]. The incompetency to prevent aging in available glassy polymers causes interest to new rigid and porous materials, known as super glassy polymers with intrinsic microporosity (PIMs). The PIMs were developed by rigid segments, which are particularly internally flexible [86]. Another concept presented from mixing both of the techniques mentioned in the above by solving the issue of polymer aging through the particular supplement of microporous microparticle, porous aromatic framework towards super glassy polymers.

Solvent casting technique may influence the crystallinity or amorphous region of the polymeric membrane along with subsequently modifies the permeability. Furthermore, the distinctions in the molecular sizes of the solvents are able to present several free volumes in the membrane manufacture process, namely, distinct solubility coefficient esteems [87, 88]. Casting solvent has an important part in the morphology of polymeric blend membranes. Demonstration of fully dense ethylene vinyl acetic acid derivation (EVA)/liquid poly(ethylene glycol) (PEG) blend membrane changes via evaporation process of solvent was done by Zamiri et al. [89]. However, a few voids had showed up in the membrane frameworks. In their study, the solvent and non-solvent for EVA were chloroform and PEG, respectively. The mixing of chloroform and PEG had dissolved the EVA, and high EVA and non-solvent PEG composition were obtained in the arrangement by continuous evaporation of chloroform upon the casted solution. Hence, the polymer precipitated together while displaying cavity. They additionally showed examples with

20 wt% of PEG; the cavity where it amplified and interconnected, hence, producing a noteworthy drop in the (CO_2/N_2) gas selectivity.

The impact of impurities at high CO_2 permeability membranes is suggestive of a sensitive problem. It usually occurs in the field condition that impacts the separation of various gas separation membranes, which will incorporate the gas flow with compressor oils from pump and presence of the water vapor in the inlet stream [90]. The event is viewed as "penetrant-induced plasticization" or in short, "plasticization" [50,51]. Often, plasticization results in increment of carbon dioxide flux but lowers the selectivity of the mixed gas (e.g., CO_2/CH_4 and CO_2/N_2) of conventional membrane materials (e.g., polysulfones, CA, polyimides), especially at high pressure. Commonly, for plasticized, glassy polymeric membranes, gas permeability diminishes with expanding feed pressure until plasticization occurs. Next, it will begin to rise with respect to pressure. For example, in CO_2 -induced plasticization in glassy polymers, regular plasticization pressures are between 10 to 35 bar for suitable polymers in gas separation applications [91]. These qualities are not equivalent to the equilibrium value for low upstream pressure with increments in time. Time-based relaxation procedure of the polymer asserted that it sources from among the non-equilibrium glassy conditions of the polymer. This demonstrates the swelling of the sorbed penetrant, thus easing the polymer matrix composite and thereby causing the suppression of glass transition temperature, T_g [92].

Three elective techniques can stifle plasticization of glassy polymers, which are temperature treatment, cross-linking of polymers, and combining with less plasticizable polymer [22, 53]. Since recent discussion on thermal treating, the second of the two will be considered thereafter. Blending usually enhances the overall properties of the polymeric membranes while decreasing the plasticization effects [93]. Transportation of a particular gas can be facilitated by tuning the blend composition which result in morphologies that are shaped [56]. On numerous occasions, a phase-separated blend is necessary for greater transport of species [94]. To increase selectivity, homogenous blends are favorable while for enhancement of permeability, appropriate type of blends is the immiscible blends. Amid the mixing procedure of immiscible blends, polymer free volume expansion caused expanded gas permeation rates. However, miscible polymer blend demonstrates a noteworthy negative volume changes in mixing. The outcome reveals a huge reduction in the rate of permeation for common gas and therefore, an expansion in gas selectivity [95, 96].

Sometimes, a union of cross-linking and blending is seen as a good achievement. For instance, the CO_2 -selective cross-linked thin-film composite poly(vinyl liquor) (PVA)/polyvinylpyrrolidone (PVP) blend membranes doped with appropriate amine carriers were combined by Mondal and Mandal [60]. Another methodology was created

as hybrid ternary blends, which implies a compatibilization of the blend constituents through the extra targeted fillers. The aspect of appropriate fillers, besides improving the mechanical properties, is inducing an impressive decline in blends' plasticization [97]. Qiu et al. [51] demonstrated that cross-linking at raised temperatures ($\sim 15^{\circ}\text{C}$ above T_g) for polyimides are able to balance out membrane in swelling and plasticization. Additionally, the plasticization pressure showed an important shift to higher pressures [98]. Mixing of GC and grafting was further revealed as one of the approaches to inhibit plasticization. Among these techniques, Achoundong et al. [99] was able to alter the CA membranes through the grafting of VTMS into hydroxyl groups to produce a cross-linked structure of the polymer.

Anti-plasticization is another phenomenon that disrupts the separation performance of polymeric membranes. The contrary conduct of plasticization impacts the polymeric membranes at low concentrations of a particular penetrant. Rather than expanding the segmental movements of polymer chains as accomplished for the plasticization, the penetrant molecule shows an induced drag in chain fluctuation, thus diminishing the diffusion of all different permeation in the membrane [100]. For example, either a decrease of segmental portability or an expanded stiffness can diminish the gas permeability, while the related selectivity was changed alternately [49]. Anti-plasticization has impacts on the TCP, PNA, and DDS of PSF and PPO membranes [101]. These extra diluents or plasticizers to the polymers have a low molecular weight that was joined by critical decreases in absorption level and the permeabilities for gases such as He, CO_2 , and CH_4 . Upon low anti-plasticizer concentration, the selectivity expanded through surpassing from an established concentration, causing a decline in the selectivity because of the substitution of anti-plasticization against the anti-plasticization impact. Another major complication in commercial glass-type polymers is the hysteresis that appears in sorption, permeation, and dilation isotherms of CO_2 . Amid feed pressurising, these properties are primarily estimated to be lower compared with those deliberated while feed depressurising. Among the features in the hysteresis, it can be considered because of a late polymer chain rearrangement in CO_2 pressure growth [102 – 104].

2.6.2 Hybrid and composite membranes

Recently, the technology of membrane gas separation technology is rapidly developing due to its diverse benefits compared with the conventional methods (primarily absorption by amines). Particularly, membrane gas separation demonstrates flexibility in operation, low operating costs, easy scale-up, and high quality of product and compact design. The most significant implementation of membrane gas separation is CO_2 capture and recovery

from the gas streams. Atmospheric concentration of CO₂ is raising significantly over the last decades. The average CO₂ concentration was identified at 399 ppm in 2015, which is around 40%, higher compared to the years of mid-1800s. Intensified carbon dioxide release was detected in the previous era with 2 ppm/year of average growth [105]. This strong rising trend is caused by the increasing demand for energy production from fossil fuels. One-third of the global energy utilization, as well as 40% of carbon dioxide emission come from the industrial sector [106]. Significant greenhouse gases impact with carbon dioxide emission as the primary perpetrator on global warming, as well as climate change, forces the capture and recovery of carbon dioxide to be a worldwide interest [107-109].

There are several types of membrane materials, namely, inorganic substance (metals, ceramics, carbons, zeolites), organic substances (glassy, polymer blends and rubbery), porous hybrid materials (zeolitic imidazolate frameworks (ZIFs), and metal-organic framework (MOFs). The MMMs were discovered by Chung et al. [110], in which they reported on an additional path for solution-diffusion transport. According to Powell and Qiao [111], nanoparticles assimilation comes with three primary impacts on the permeability of membrane, for example, the ability to modify permeability by acting as molecular sieves, the ability to increase permeability by disturbing the structure of the membrane matrix, and the ability to lower the permeability by acting as a barrier. Other relations are also suggested for the purpose of describing the properties of gas transport in MMMs, for example, the Higuchi model [112] and the three-phase Maxwell model [113]. The mentioned models are naturally complex without providing significant improvement in their results compared with the two-phase Maxwell equation. On a small scale, restrictions of selectivity and permeability can be overcome via the use of inorganic membranes; however, it requires high costs for the production of inorganic membranes (some magnitude higher than the cost for polymeric membranes).

In addition, inorganic membranes production in a large scale requires enhancements in its reproducibility. The principle of MMMs merges the selectivity and size/shape of nanoporous materials with mechanical stability and processability of polymers [114]. The advantages of the combination of polymeric and inorganic components are that MMMs can be taken into account as an evolutionary method to elevate both the selectivity and the permeability. Gas permeance via MMM is determined by both polymer and inorganic filler properties of intrinsic molecular sieve [115]. Benefit of MMMs can be found in its greater properties of gas separation contributed by the molecular inorganic filler that provides the ability to sieve molecules. Inorganic particles utilized in MMMs are divided into two which are porous and non-porous; for example, CMS, metal oxides, non-porous silica and porous zeolites. Zeolites are well known to be recognized as the leading edge

molecular sieve family utilized in MMMs [116]. Zeolites are crystal-like particles with three-dimensional (3D) and uniform micropore structures, and interconnected cages and tunnels in order for the gas molecules to be sieved according to the desired shapes and sizes [117]. Zeolite addition in the discerning skin layer improves the selectivity of CO₂/CH₄ to about half, compared with the neat hollow fibers made up of PSf/Matrimid® [118].

Incorporation of CMSs were also done [114], whereby its construction were carried out with highly porous ingredients to allow for high permeability of gas; however, its molecular structure of sieving pore offers gas penetrants discrimination to give high selectivity [73, 119]. Studies by Barsema et al. [120] introduced the incorporation of CMS fiber into two different polymer, namely Ultem®1000 and Matrimid®5218. For membrane made up of Matrimid® 5218-CMS, CO₂/CH₄ selectivity increases by 45% in accordance with the pristine Matrimid® 5218 membrane. Meanwhile, Ultem®1000-CMS observed 40% increment for selectivity of CO₂/CH₄, which was in accordance to Ultem® 1000 membrane. Moreover, MMM with carbon nanotubes (CNTs) has also become an attractive research field.

Another significant inorganic particle type is if the metal oxide nanoparticles have a great affinity to CO₂ [121]. Hosseini et al. [122] incorporated nanosized MgO with Matrimid® polymer prior to ten days of treatment with silver ion in nanocomposite membrane preparation. The best separation performance of CO₂/CH₄ increased to 50%, which is in accordance to the neat membrane of Matrimid®. Separation of CO₂/CH₄ in nanocomposite membrane are through solution-diffusion mechanism combination in the polymer matrices with size exemption by silver covered MgO, as well as assisted the transportation through MgO/Ag and CO₂ interaction [123]. The MOFs are anticipated to favor the organic phase over the inorganic fillers, as organic linkers in MOFs have better affinity with polymer chains. The ZIF-90 possesses sodalite cage-like structures with size of pore of 0.35 nm. In addition, carboxyl groups in particle ZIF-90 have a good CO₂ affinity via a non-covalent chemical interaction. Permeability of CO₂ increased from 390 to 720 Barrer when polyimide 6FDA-DAM membrane was incorporated with ZIF-90. Selectivity of CO₂/CH₄ increased from 27 to 37, which indicates that the MMM is defect-free [117]. Meanwhile, the ZIF-8 has a facile synthesis, as well as good thermal and chemical stability, making it an attractive member of MOFs. Both had improved the CO₂/CH₄ selectivity as well as the CO₂ permeability, as perceived for the membranes of ZIF-8/Matrimid® [124].

Inorganic particles that are non-porous, for instance, silica, are used in membranes of nanocomposite structures [53, 86]. Previous works stated that the additional void located at the interface between silica agglomerates and the polymers has the probability to

induce permeability enhancement [114, 125, 126]. Sadeghi et al. [127] studied CH₄ and CO₂ properties of transport through composite membrane made of silica and polybenzimidazole (PBI). They identified the solubility enhancement of the condensable gases as the hydrated silica particles was incorporated due to an increment in the amount of hydroxyl groups in the polymer matrix. Ruling mechanism of gas permeance transformed from the mechanism of diffusion in the neat PBI membrane into mechanism of solution in the hybrid membrane. Permeability for non-condensable gas was also found to be decreased. This is due to gas diffusivity reduction in the polymer matrix affected by limited gas molecules motion in the company of silica particles. One primary challenge in MMMs development is the ability for the inorganic nanoparticles to disperse across the polymer matrices.

Generally, nanoparticles scatter below par in the polymer matrix, making them to be more likely to aggregate in the MMM formed which leads to the establishment of various stress under the act of forces from outside, hence weakening the stability performance of the materials, particularly at high concentrations of inorganic filler [128]. Zeolites addition to glassy polymer usually causes defects formation at the polymer-zeolite interface due to poor polymer matrix and zeolites compatibility. This issue has the ability to seriously deteriorate the performance of membrane separation. As an example, MMM constructed from Matrimid®-zeolite exhibited higher permeability and no selectivity enhancement in accordance to the neat membrane of Matrimid® caused by voids formation which is delaminating away. In the application for sweetening of natural gas, inlet gas is normally gained from the gas well at 20-70 bar of typical pressure and less than 8% of CO₂ content. The content of CO₂ needs to be decreased to around 2% in order to condone to pipeline requirements and specifications for transportation.

Although gas permeation membranes usage in improved recovery of oil process at elevated partial pressure of CO₂ is considered to be successful, the usage of dense membranes and certain membranes of porous inorganic structure, for example, CMS at low partial pressure of CO₂ is deemed as unsuccessful. This is mainly caused by significant hydrocarbon loss within the CO₂-rich permeate, as permeability are in contrast with selectivity. Hydrocarbon loss causes the process to be economically unattractive. However, combination of a hollow fiber gas liquid membrane contactor and acid gas absorption as a substitute to dense membranes obtains higher selectivity of separation and is deemed as more attractive in the applications of natural gas sweetening; particularly to minimize the loss of hydrocarbon in situations with low concentration of CO₂. Various studies were conducted through the utilization of this process of membrane and chemical absorption in order to separate the CO₂. However, most works were done under low membrane pressure (≤ 2 bar), primarily to highlight the separation of CO₂ from gaseous

blends in the applications of flue gas without the involvement of pressurized gas stream [129]. This is because the membranes of microporous polymeric structures are naturally delicate, which limits their utilization in harsh pressure condition. Thus, in the case of natural gas sweetening involving operation under high feed pressure, numerous research on membrane contactor module construction, operation condition and materials are needed to review the membrane gas-liquid contactors potential for high pressure usage.

Nowadays, available works on high pressure membrane contactors are not enough with only two reported works can be found, which is by Dindore et al. [130] over a decade ago and by Marzouk et al. [131] in 2010. Both researches described the gas side pressure as having extended impact on carbon dioxide flux for physical absorption compared with chemical absorption, making physical absorption more suitable for high pressure usage than its use in low pressure usage. At high pressure and temperature, inorganic membranes are favored due to its exceptional stability in terms of chemical, thermal, and mechanical aspects, high pressure stability, and good erosion resistance over the conventional polymeric membranes. In addition, inorganic membranes also possess regeneration potential after fouling primarily caused by its relatively robust chemical and mechanical structures. In general, pore plugging is a normal concern for all membrane types. However, plugging of pore is not seen as a primary issue in small scale experiment, where cleaned gas is utilized. However, gas feed usually contains particles in industrial operations, which in numerous cases require the pretreatment of feed gas.

3. Research gaps

Commercialization of polymeric membranes for gas separation began years ago. These systems have gained increased research interest due to its simplicity and low-energy intake. Gas separation is required in numerous processes in the refinery, for example, in the capture of carbon dioxide, treatment of natural gas, separation of hydrocarbons and purification of hydrogen. Membranes in these processes have potential to be substituted with the existing techniques of pressure swing adsorption, amine scrubbing, as well as cryogenic distillation. This chapter discusses the implementations of polymer membranes in the refinery through commercialized units and current materials reviews. Economical assessment of the membranes involved in contrast to the traditional processes is also included. Average permeance calculation offers reasonable results as only one of the gases' permeance is altered. If alteration of permeance for each gas was done during the separation process, proper extraction of the required membrane area cannot be attained. Thus, the effects of permeance parameters need to be considered during the minimization of overall and operation costs, and energy usage, if the behavior of variable permeance was perceived in the module of the membrane.

It is assumed that the separation process of membrane will be regularly utilized as the future practical biogas enhancement technology. High purity and high CH₄ gas recovery can be attained using a two-step membrane process. Permeance and CO₂/CH₄ selectivity enhancement could further decrease the capital cost of gas separation by membrane. Certain conundrums are required to be investigated or resolved in the future, which are:

- > Systematic investigation on the effect of membrane materials and operation conditions on the operating cost with predetermined purity and recovery of products that are still lacking. Thus, enhancement of systematic investigation for biogas involving optimal operating cost and fixed separation target are immediately required;
- > More upgrades in membrane permeance or selectivity might not result to extra advantages for biogas enhancement. Systematical investigations on the effect of membrane permeance, membrane selectivity, operating pressure towards energy consumption, operational cost, and capital cost are essential in understanding the required permeance and selectivity of a membrane with optimal cost of operation;
- > Detailed investigation should be conducted on two-step membrane process, as it is the optimum process that can be done to achieve CH₄ concentration above 97% and above 98% for CH₄ recovery, both of which are attractive parameters for the production of biomethane;
- > If any significant changes of the gases' permeance during membrane separation process are identified, calculation of membrane permeance in membrane process needs to be attuned as per the precise operating condition.

4. Future perspectives

The technology of membrane separation has the most potential in capturing CO₂ from flue gas according to the advantageous of membrane processes, such as operation simplicity, small footprint, modular construction, and zero emission of hazardous by-product. Nevertheless, utilization of membrane process to CO₂ capture from flue gas is still under further discussion, as the separation aims suggested by the United States Department of Energy for product with recovery of more than 90% and purity of 95% and higher are very hard to obtain through low cost of capture and energy consumption. Low concentration of CO₂ and low flue gas pressure are accountable for the struggle in separation process primarily due to high consumption of energy and the cost of capture. Numerous researchers have optimized the membrane-based processes to separate the carbon dioxide from flue gas mixture with the intention to search for optimum operating parameters and appropriate materials with the lowest cost and energy consumption [132-135]. CO₂ concentration in the flue gas of power plants is low (approximately 13% to

15% for the usual coal fired power plant) brought the most vital challenges for the capture of CO₂ process. Castel et al. [136] reported 10% of feed gas CO₂ concentration requires the amount of energy intake for membrane system that is too high to be acknowledged, although having selectivity of higher than 120. As concentration of CO₂ in inlet feed surpassed 20%, the energy intake for the membrane system is reduced making the membrane process to be more economical than the old absorption process. As for the usual case of 60 selectivity with 30 mbar downstream pressure, membrane system with single stage is able to fulfill 0.7 MJ/kg energy requirement for 20% of CO₂ feed gas. Thus, decreasing concentration of CO₂ in flue gas is the primary blockage in realizing the low capture cost of 20 \$/ton CO₂. Systematic analysis of techno-economic was conducted in order to establish an ideal membrane material offering optimal operating and capital costs for the membrane system.

Membrane permeance and selectivity were identified according to the Robeson upper limit for separation of CO₂/CH₄ via membrane. Usually, attractive area is found in the vicinity of the upper bound or surpassing the Robeson upper limit. As for the two-stage membrane process, minimum cost of operation for fixed CH₄ purity of 96%, as well as fixed CH₄ recovery of 85% was detected. Increment in the selectivity of CO₂/CH₄ initially reduces the operating cost followed by increasing operating cost during the latter half. Cost of 0.037 \$/Nm³ for separation process is calculated in the event that the optimal membrane with selectivity range of 10 to 25 and operating pressure ratio of 10 under high permeance of CO₂ of above 2000 GPU. As the optimal membrane is confirmed, the cost of biogas upgrades is controlled by the compressor, comprising the utility expenses and capital depreciation, which totaled to roughly 85% of the total cost. Furthermore, more reduction in the membrane skid cost reduces the operating cost and increases the CO₂/CH₄ selectivity with minimized cost of operation. Lastly, single step gas separation membrane has higher operating cost than two-stage membrane with optimal selectivity.

It is ideal for membranes to possess high CO₂ permeability with sufficient CO₂/CH₄ selectivity (10–25) [137]. Polyethersulfone (PESU) membrane with 35.5 selectivity of CO₂/CH₄ is sufficient for biogas enhancement of the membrane process with two-step. The effect of CO₂/CH₄ selectivity as well as the area of membrane towards separation performance was investigated by Makaruk et al. [138]. Investigation on biogas enhancement with the flow rate of feed gas of 1000 Nm³/h, methane concentration of feed gas of 60%, as well as product gas of 98% methane was conducted. Energy usage in biogas upgrades to natural gas replacement was about 0.3 kWh/Nm³ which is equal to 1.08 MJ/Nm³. Results produced indicates increment in membrane area which contributes to relatively higher recovery of product. Nevertheless, if a very high recovery of nearly

100% were to be attained, it is anticipated that more areas of the membrane will be utilized. As lower selectivity of CO₂/CH₄ membrane is employed, higher consumption of compression power can be observed to obtain similar recovery of methane. Utilization of CO₂/CH₄ with selectivity greater than 50 could only slightly reduce the energy consumed. In this reference, the process of membrane gas separation has the ability to offer sufficient flexibility to maintain high recovery of product while the biogas process is upgraded.

Membrane system application is rising in the industry due to unique features provided by the membrane. Membrane separation process has simple installation procedure with minimum supervision required compared to other separation processes [139]. Moreover, it utilizes less space with no moving parts making maintenance as not one of its crucial needs [140]. Additionally, it consumes less energy as well as is deemed as a technology that is environmentally friendly due to the involvement of no gases emission and solvents [18]. Scaling up the membrane for commercialization purposes is also an easy task. According to its material, membranes are divided into polymeric, inorganic, and metallic. Platinum or palladium made metallic membranes have exceptional performance; however, the precious metals cost highly affect the selection of the membranes. Inorganic membranes are recognized as good substitutes, having better chemical stability and lower cost of fabrication. However, elevated temperature between 200°C and 900°C is required in the operation of inorganic membranes [8]. Lately, polymeric membranes are a hit in the industries due to its competitive performance and outstanding economy [107]. Operation of the membranes is done at environment temperature and they possess excellent properties. In 1960s, polymeric membranes revolution began as Loeb and Sourirajan [141], which fabricated a membrane using CA for water desalination through reverse osmosis. The membrane was 0.2 µm thick, supported on a porous substrate with capability of transforming seawater into potable water.

Conclusion

Most of the polymer membranes utilized in the gas separation processes that is membrane-based exhibit low thermal resistance. In various implementations, working at elevated temperatures is essential. Alternatively, high stability membranes could offer new application fields through prolonged membrane lifetime at high temperatures. In fact, in terms of energy and cost saving, it is important for the operation of the membranes to be conducted at the highest permissible temperatures. Presently, most systems of gas separation need an effective heat exchanger to reduce the influence of the membrane temperature to less than 50°C. Such requirement indicates operating cost and extra capital demands during operation with a hot stream. Furthermore, expensive cost

related to the novel raw materials and low processing ability of thermally stable polymers restricted their commercialization to the comparatively dedicated gas separation field. Development of polymeric membranes separation performance for CO₂ separation industry is broad research area due to membranes competition with other separation technology in terms of technological, economic, environmental, and safety aspects. Certainly, one the most significant aspect in membrane gas separation processes is proper material selection. Improvement of polymer membranes with higher selectivity and permeance reassures the concerns on high membrane technology cost. Hence, existing efforts should focus on eliminating them through the introduction of new polymer membranes with high CO₂ permeability, combined with good chemical and physical stability, as well as acceptable level of selectivity. Certain stimulating concerns in utilization of these materials for membrane fabrication has gained interests from academicians. Primary concerns in this matter are the pressure and thermal conditioning, chemical and physical aging, permeation hysteresis, plasticization, impurities or existence of trace contaminants, and casting solvent. In a nutshell, this chapter compiles all of the reviewed papers that particularly focused on enlightening the challenging issues that influence the CO₂ separation properties of conventional polymeric membranes.

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